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Spin–lattice relaxation dispersion in polymers: Dipolar-interaction components and short- and long-time limits

A. Gubaidullin [a], T. Shakirov [a], N. Fatkullin [a], R. Kimmich [b,*]

[a] Department of Physics, Kazan State University, Kazan 420008, Tatarstan, Russia
[b] University of Ulm, Sektion Kernresonanzspektroskopie, 89069 Ulm, Germany

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ABSTRACT

The Mori–Zwanzig projection operator technique was employed to derive the effective Hamiltonian for spin-segment coupling. The fluctuations of this operator are responsible for spin–lattice relaxation in polymer chains. In detail, dipolar interaction of spins is rigorously analyzed by components representing fluctuations of the Kuhn segment end-to-end vectors and local fluctuations on a length scale shorter than the root mean square Kuhn segment length. The former correspond to the usual coarse-grain picture of polymer chain mode theories. It is shown that these non-local chain modes dominate proton spin–lattice relaxation dispersion of flexible polymers at frequencies up to about 10^8 Hz. A corresponding evaluation of experimental data for polybutadiene melts is presented.

1. Introduction

Polymer chain dynamics is usually described by a linear superposition of chain relaxation modes expected to be relevant in the limit $t \gg \tau_s$, where τ_s is the Kuhn segment fluctuation time [1–3]. This time limit is equivalent to the length scale $l \gg b$ of the moving entities, where b is the root mean square end-to-end length of Kuhn segments which typically is ≈ 1 nm for flexible polymers. Instead of "Kuhn segment" the term "Rouse subchain" is often used in an attempt to distinguish conformational from dynamic properties. In any case, the values reported in the literature for these two species of model chain segments do not differ very much.

A point is that the definition of Rouse subchains anticipates a Gaussian end-to-end statistics whereas this assumption is not required in the definition of Kuhn segments. Nevertheless it is possible to prove rigorously that fluctuations of Kuhn segments (with non-Gaussian end-to-end statistics) in any ideal non-entangled chain lead to exactly the same initial decay of the binary normal-mode correlation functions as predicted by the formalism based on Rouse subchains (unpublished results; see also [4]). In this sense, the term "Kuhn segment" is less restrictive than "Rouse subchain", and is therefore preferable.

The question is then how dynamics in the opposite limits, i.e. $t \leqslant \tau_s$ and $l \leqslant b$, respectively, can be described, and how chain modes in the proper sense can be distinguished from intra-segmental ("local") fluctuations [5,6]. This is the subject of the present study.

Although a polymer chain as a whole must be considered as a single dynamic entity subject to a series of superimposed modes, different length scales of the modes contributing to chain motions must be distinguished. Fast modes will be connected with short length scales relative to Kuhn segments and slow modes are related to long length scales. Qualitatively one therefore expects that short-time fluctuations are of a more local nature whereas long-time fluctuations more or less extend over the whole chain.

The objective is to analyze proton spin–lattice relaxation in polymer melts by interaction components the fluctuations of which correspond to "local" and "non-local" molecular motions. Normally the origin of proton spin–lattice relaxation is thermal fluctuation of dipole–dipole coupling of spins. Dipolar interaction of two spins numbered by the subscripts i and j is described by the Hamiltonian $\hat{H}_{ij}(t)$ the time dependence of which originates from the thermally fluctuating inter-nuclear vector $\vec{r}_{ij} = \vec{r}_{ij}(t)$. The analytical form of the dipolar-interaction operator to be discussed below stipulates a non-trivial correspondence of "local" and "non-local" motions on the one hand and on the other hand the space sections (particularly with regard to the solid angle) covered by fluctuations of $\vec{r}_{ij} = \vec{r}_{ij}(t)$ on "short" and "long" time scales.

Obviously the analysis of different components of collective valence-bond motions contributing to spin–lattice relaxation in polymers is a multi-faceted problem. To summarize, in any

* Corresponding author. Fax: +49 731 24281.
E-mail address: rainer.kimmich@uni-ulm.de (R. Kimmich).

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